

E-Content Study Material

B. Sc. Chemistry (H)

2nd Year

Paper II B

Inorganic Chemistry

Chapter VII: Acids and Bases

Topic: Solvent-System Concept of Acids and
Bases

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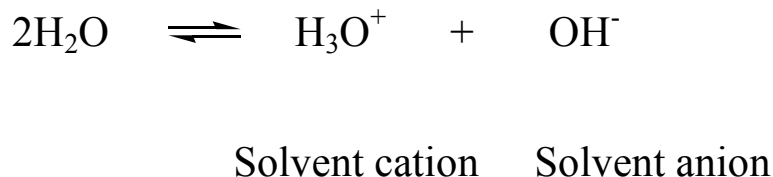
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Solvent-System (or Autoionization) Concept of Acids and Bases.

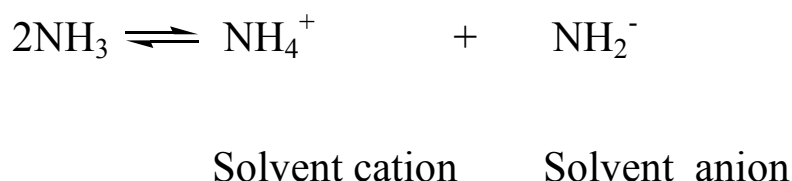
According to solvent-system concept put forth by Franklin, an acid is a substance which, in a solvent, increases the concentration of a cation characteristic of that solvent and a base is a substance which, in a solvent, increases the concentration of an anion characteristic of that solvent. The characteristic cations and anions of the solvent are the ions produced during its autoionization.

Autoionization of water, for instance, is represented as

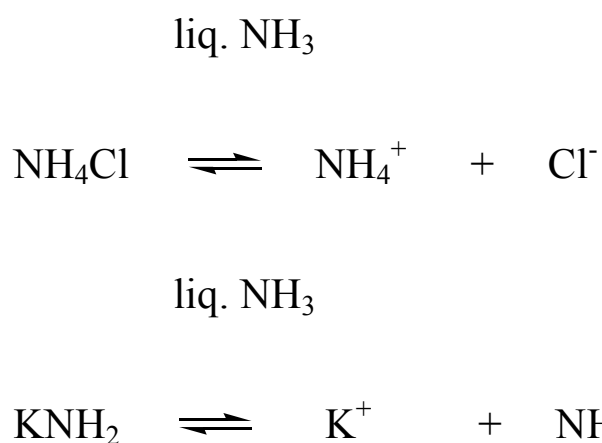


Thus, in water, substances giving H_3O^+ ions are acids and those giving OH^- ions are bases.

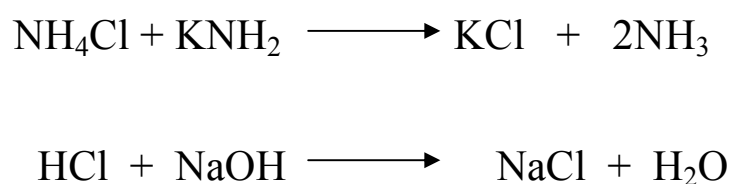
Liquid ammonia undergoes autoionization as follows:



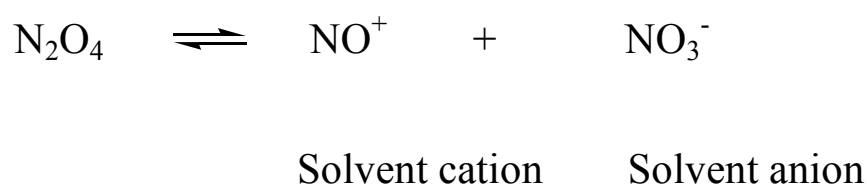
According to solvent-system concept, in liquid ammonia, substances which give ammonium ions (NH_4^+) act as acids while those giving amide ions (NH_2^-) act as bases. For example, ammonium chloride acts as an acid while potassium amide acts as a base in liquid ammonia.



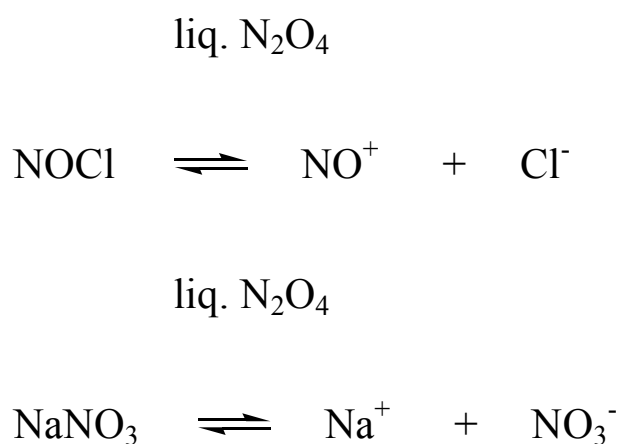
The acid-base neutralisation reaction of NH_4Cl and KNH_2 in liquid NH_3 is analogous to that of HCl and NaOH in water.



Consider the autoionization of liquid nitrogen tetroxide:



According to solvent-system concept, in liquid nitrogen tetroxide, the substances which furnish nitrosyl ions (NO^+) behave as acids and those which furnish nitrate ions (NO_3^-) behave as bases. Accordingly, NOCl behaves as an acid and NaNO_3 behaves as a base, in this solvent.



Autoionization of sulphuric acid is represented as



Thus, any species giving H_3SO_4^+ ion acts as an acid and any species giving HSO_4^- ion acts as a base.

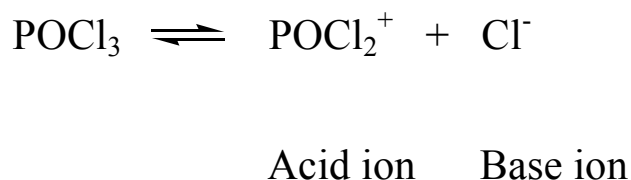
Just as ionic product of H_2O is written as $K_w = [\text{H}_3\text{O}^+] [\text{OH}^-]$, similarly, the ionic product of any solvent AB ionising as $\text{AB} \rightleftharpoons \text{A}^+ + \text{B}^-$, may be written as $K_{AB} = [\text{A}^+] [\text{B}^-]$. Just as the convenient

scale for indicating H^+ ion concentration in aqueous media is the pH scale and the point of neutrality is given by $-1/2 \log K_w$ (i.e., $pH = 7$), similarly, we can construct a convenient scale for indicating the acidity of the solvent AB , the point of neutrality being given by $-1/2 \log K_{AB}$.

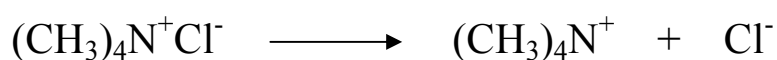
Limitations of Solvent-System (or Autoionization) Concept).

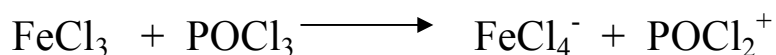
The solvent-system concept lays too much stress on ionic reactions and chemical properties of the solvent. This concept totally ignores the physical properties of the solvent. The limitations of the concept can be understood more clearly by taking into consideration certain specific examples.

Solvent $POCl_3$ undergoes autoionization as

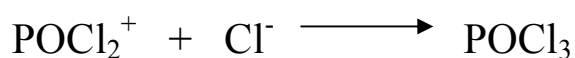


In $POCl_3$, $(CH_3)_4N^+Cl^-$ and $FeCl_3$ ionise as follows:





According to the solvent-system concept, therefore, $(\text{CH}_3)_4\text{N}^+\text{Cl}^-$ is a base and FeCl_3 is an acid in POCl_3 and the reaction between these two species is a typical neutralisation reaction which may be represented as



Acid ion Base ion

The above view receives support from the fact that FeCl_3 can be titrated quantitatively against

$(\text{CH}_3)_4\text{N}^+\text{Cl}^-$ in POCl_3 as the solvent conductometrically as well as spectrophotometrically and the end point is sharp.

The same reaction occurs between FeCl_3 and $(\text{CH}_3)_4\text{N}^+\text{Cl}^-$ in $\text{OP}(\text{OEt})_3$ as the solvent giving the same product FeCl_4^- . However, this solvent cannot autoionize to give Cl^- ion. In fact, there is no evidence for the autoionization of the solvent $\text{OP}(\text{OEt})_3$ at all. The solvent-system concept thus fails to explain the reaction between FeCl_3 and $(\text{CH}_3)_4\text{N}^+\text{Cl}^-$ in $\text{OP}(\text{OEt})_3$.

Autoionization of liquid SO₂ is supposed to occur as follows:



Acid ion Base ion

The compound SOCl₂ is supposed to ionize in liquid SO₂ as follows:

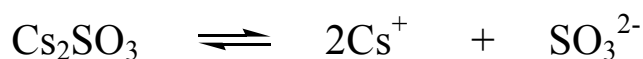
liq. SO₂



According to the solvent-system concept, therefore, SOCl₂ is an acid.

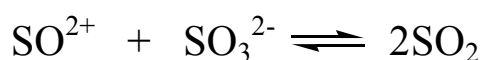
Cs₂SO₃ ionises in liquid SO₂ as follows:

liq. SO₂



According to the solvent-system concept, therefore, Cs₂SO₃ is a base.

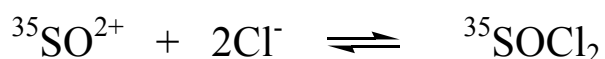
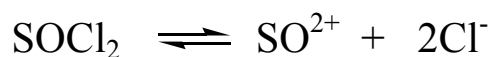
Evidently, the net reaction between SOCl₂ and a sulphite would be a neutralisation reaction as per the solvent-system concept.



Such a reaction does occur between SOCl₂ and Cs₂SO₃.

The explanation for the above reaction is, obviously, based on the autoionization of liquid SO₂. But, autoionization of liquid SO₂ has not been established at all. Liquid SO₂ has a very low dielectric constant which does not favour its ionization. Nonionization of liquid SO₂ is fully supported by the following experiment:

SOCl₂ is dissolved in liquid SO₂ labelled with radioactive ³⁵S. According to the solvent-system concept, the following reactions are supposed to occur:



If autoionization of liquid SO₂ actually occurs, the labelled and unlabelled SO²⁺ ions would compete with each other to combine with the Cl⁻ ion to form SOCl₂. As a result, a considerable amount of ³⁵S would get incorporated in SOCl₂ within a very short time. But this does not happen. The half-life for the exchange of ³⁵S in this reaction is found to be about 2 years. This rules out the possibility of

autoionization of liquid SO_2 . In other words, the reaction between SOCl_2 and Cs_2SO_3 cannot be explained on the basis of solvent-system concepts.

It may thus be concluded that the solvent-system concept is useful only when the ionic species formed in solutions are definitely known. The concept should not be stretched for solvents which are not conductive towards ion formation and also for solvents the nature of whose ions or even the existence of whose ions is not definitely known.